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FUNDAMENTAL PROCESSES OCCURRING AT ELECTRODES(U)
CALIFORNIA INST OF TECH PASADENA DIV OF CHEMISTRY AND
CHEMICAL ENGINEERING F C ANSON 09 JAN 84

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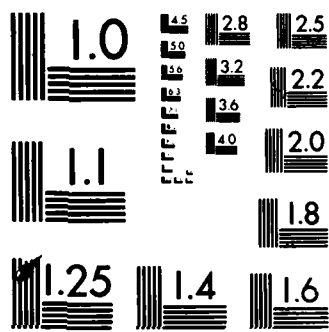
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The ARO-supported research in electrochemistry carried out in our laboratory during the last three year period has focused on the behavior of electrodes coated with polyelectrolytes. Various redox couples were incorporated by ion-exchange into the coatings where their electrochemical responses were observed and analyzed. The objectives have been to measure charge propagation rates and cross reaction rate constants for the incorporated reactants which were also tested as electrocatalysts. Most of the results have been summarized in the publications that have resulted from the research. Abstracts from several of these are presented in the body of the report.

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FUNDAMENTAL PROCESSES OCCURRING AT ELECTRODES

Final Report

Fred C. Anson

May 1, 1980 - October 31, 1983

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New Model for the Interior of Polyelectrolyte Coatings on
Electrode Surfaces. Mechanisms of Charge Transport
through Protonated Poly(L-lysine) Films Containing
 $\text{Fe}^{\text{III}}(\text{edta})^-$ and $\text{Fe}^{\text{II}}(\text{edta})^{2-}$ as Counterions

Fred C. Anson, Jean-Michel Saveant and Kiyolaka Shigehara

ABSTRACT

A model is proposed for the interior of a swollen, polycationic coating equilibrated with a supporting electrolyte solution containing both electroactive and electroinactive counteranions. The coating is divided (conceptually) into two regions. The first, termed the "Donnan domains", represents the region where the counterions are confined by electrostatic forces; the second comprises the remaining volume of the coating that is assumed to be occupied by the supporting electrolyte solution. Some expected effects of this two-part structure on the electrochemical responses obtained in both steady-state and transient experiments with coated electrodes are discussed and compared with experimental results obtained with the $\text{Fe}^{\text{III}}(\text{edta})^-/\text{Fe}^{\text{II}}(\text{edta})^{2-}$ redox couple. The polycationic coatings employed were prepared from protonated poly(L-lysine) deposited on graphite electrodes. This particular combination of polyelectrolyte and incorporated redox couple yields rates of propagation of charge through the coating that are remarkably high in both of the regions, indicating that the open, swollen structure of the coating is particularly favorable for rapid motion of counterions. The coupling between the two propagation pathways by means of electron exchange is also quite rapid. The experimental data adhere well to the predictions of the equations derived on the basis of the two-phase model which may prove generally applicable to electrodes bearing polyelectrolyte coatings.

ELECTROSTATIC BINDING OF ANIONS AND CATIONS TO GRAPHITE
ELECTRODES COATED WITH A POLYELECTROLYTE CONTAINING
BOTH POSITIVE AND NEGATIVE FIXED CHARGES

Hans-Rudolf Zumbrennen and Fred C. Anson

ABSTRACT

Graphite electrodes were coated with a polyelectrolyte based on poly(*r*-vinylpyridine). Three types of charged groups were introduced in the polymer to vary its net ionic charge: Protonated pyridinium cations, quaternized pyridinium cations and pentacyanoferrate anions. The charge carried by the $\text{Fe}(\text{CN})_5$ groups (2- or 3-) was controlled electrochemically so that the net charge of the coatings could be varied continuously between polycationic and polyanionic states. The equilibrium incorporation of multiply-charged electroactive ions by the resulting coatings was measured as a function of the net charges of the polyelectrolyte. Preferential intra-polymer charge compensation by interaction between fixed anionic and cationic sites was demonstrated in this way.

KINETICS OF ELECTRON-TRANSFER CROSS-REACTIONS WITHIN
REDOX POLYMERS. COATINGS OF A PROTONATED POLYLYSINE
COPOLYMER WITH INCORPORATED ELECTROACTIVE ANIONS

Fred C. Anson, Takeo Ohsaka and Jean-Michel Saveant

ABSTRACT

The kinetics of the cross-reaction between $\text{Co}(\text{tpy})_2^{2+}$ (tpy = 2,2',2''-terpyridine) and $\text{Mo}(\text{CN})_8^{3-}$ or $\text{W}(\text{CN})_8^{3-}$ were measured within coatings of a protonated poly-L-lysine copolymer on rotating graphite disk electrodes. The anionic octacyano complexes were bound electrostatically within the polycationic coatings. The $\text{Co}(\text{tpy})_2^{2+}$ was dissolved in the solution that occupied the pores within the swollen coatings. The kinetic data were compared with the predictions of a recent theoretical analysis of reversible cross-reactions in electrode coatings and good agreement was obtained. The magnitudes of the cross-reaction rate constants evaluated from the data were remarkably similar despite a large difference in the equilibrium constants for the two cross-reactions. Some possible reasons for this behavior are examined.

SHIFTS IN REDOX FORMAL POTENTIALS ACCOMPANYING THE INCORPORATION
OF CATIONIC COMPLEXES IN PERFLUOROPOLYCARBOXYLATE AND POLYSULFONATE
COATINGS ON GRAPHITE ELECTRODES

Yu-Min Tsou and Fred C. Anson

ABSTRACT

The formal potentials of several redox couples incorporated in coatings of a perfluoropolycarboxylate on graphite electrodes were measured and compared with the formal potentials of the same couples in homogeneous solution. The differences observed agreed with those calculated from the Nernst equation with the independently measured incorporation coefficients for both halves of the redox couples. The dependences of the shifts in formal potentials on the nature of the incorporating complex ion, the ionic strength and the temperature were determined and indicated that the incorporation equilibrium are governed by electrostatic and hydrophobic interactions that act in opposite directions. The incorporation of most cations examined was driven by large increases in entropy that overcame the usually unfavorable enthalpy changes.

NEW STRATEGIES FOR ELECTROCATALYSIS AT POLYMER COATED ELECTRODES.
REDUCTION OF DIOXYGEN BY COBALT PORPHYRINS IMMOBILIZED IN
NATION COATINGS ON GRAPHITE ELECTRODES

Daniel A. Buttry and Fred C. Anson

ABSTRACT

A new method for introducing porphyrin molecules into Nafion coatings on electrodes is described. The incorporated porphyrins are exceptionally stable and can readily be metallated while remaining in the coating. Coatings containing cobalt tetraphenylporphyrin (CoTPP) were prepared to exemplify the method which is applicable to a variety of macrocyclic ligands possessing basic sites. The CoTPP in the Nafion coatings retained its ability to catalyze the electroreduction of dioxygen when the electrons were carried from the electrode to the almost immobile catalyst sites by $\text{Ru}(\text{NH}_3)_6^{2+}$ ions also incorporated in the coating. The resulting separation of the catalytic and electron transport functions within such coatings is argued to have general virtues that may be exploited to extend the range of applicability of polymer-coated electrodes in electrocatalysis and to diagnose the mechanisms by which they operate.

ENHANCEMENT OF CHARGE TRANSPORT RATES BY REDOX CROSS REACTIONS
BETWEEN REACTANTS INCORPORATED IN NAFION COATINGS

Daniel A. Buttry, J. M. Saveant and Fred C. Anson

ABSTRACT

The rate of charge transport within Nafion coatings by $\text{Co}(\text{tpy})_2^{3+}$ ($\text{tpy} = 2,2',2''\text{-terpyridine}$) is enhanced when it is measured in the presence of $\text{Ru}(\text{NH}_3)_6^{2+}$ with which it undergoes a rapid electron transfer cross-reaction. Similarly, the presence of $\text{Cp}_2\text{FeCH}_2\text{N}(\text{CH}_3)_3^{2+}$ ($\text{Cp} = \text{cyclopentadienide}$) enhances the propagation rate of $\text{Co}(\text{tpy})_2^{2+}$. Cyclic voltammetry was used to demonstrate the effect qualitatively and chronocoulometry to document it quantitatively. The enhancement results because electron transfer between the more slowly diffusing complex ($\text{Co}(\text{tpy})_2^{3+}$ or $\text{Co}(\text{tpy})_2^{2+}$) and the more rapidly diffusing $\text{Ru}(\text{NH}_3)_6^{2+}$ or $\text{Cp}_2\text{FeCH}_2\text{N}(\text{CH}_3)_3^{2+}$ complexes allows the latter to carry charge between the electrode surface and the slower moving complex. A formula for the extent of the enhancement is derived for the case of potential step chronocoulometry or chronoamperometry and used to compare calculated enhancements with those measured experimentally. Some implications of electron transfer enhancement of charge propagation rates for electrocatalytic applications with polymer coated electrodes are pointed out.

LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP
DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:

Electrochemical Responses of Multiply-charged Transition Metal
Complexes Bound Electrostatically to Graphite Electrode Surfaces
Coated with Polyelectrolytes

Noboru Oyama, Takeshi Shimomura, Kiyotaka Shigehara and
Fred C. Anson
J. Electroanal. Chem., 112, 271 (1980)

Kinetic Behavior to be Expected from Outer-Sphere Redox Catalysts
Confined within Polymeric Films on Electrode Surfaces

Fred C. Anson
Journal of Physical Chemistry, 84, 3336 (1980)

Evaluation of Rate Constants for Redox Self-exchange Reactions from
Electrochemical Measurements with Rotating Disk Electrodes Coated
with Polyelectrolytes

Kiyotaka Shigehara, Noboru Oyama and Fred C. Anson
Inorganic Chemistry, 20, 518 (1981)

Electron Hopping vs. Molecular Diffusion as Charge Transfer Mechanisms
in Redox Polymer Films

Daniel A. Buttry and Fred C. Anson
J. Electroanal. Chem., 130, 333 (1981)

Electrochemical Control of the Luminescent Lifetime of $\text{Ru}(\text{bipy})_3^{2+}$
Incorporated in Nafion Films on Graphite Electrodes

Daniel A. Buttry and Fred C. Anson
J. Amer. Chem. Soc., 104, 4824 (1982)

Apparent Diffusion Coefficients and Electron Propagation Mechanisms
in Viologen Polyelectrolyte Coatings Containing Multiply-Charged Anions

Roger J. Mortimer and Fred C. Anson
J. Electroanal. Chem., 138, 325 (1982)

Diffusional Pathways for Multiply-Charged Ions Incorporated in
Polyelectrolyte Coatings on Graphite Electrodes. $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$
in Coatings of Protonated Polylysine

Fred C. Anson, Takeo Ohsaka and Jean-Michel Saveant
J. Phys. Chem., 87, 640 (1983)

Effects of Electron Exchange and Single File Diffusion on Charge
Propagation in Nafion Films Containing Redox Couples

Daniel A. Buttry and Fred C. Anson
J. Amer. Chem. Soc., 105, 685 (1983)

Self-Exchange Reactions at Redox Polymer Electrodes. A Kinetic
Model and Theory for Stationary Voltammetric Techniques

Fred C. Anson, Jean-Michel Saveant and Kiyotaka Shigehara
J. Phys. Chem., 87, 214 (1983)

New Model for the Interior of Polyelectrolyte Coatings on Electrode Surfaces. Mechanisms of Charge Transport Through Protonated Poly(L-Lysine) Films Containing $\text{Fe}^{\text{III}}(\text{edta})^-$ and $\text{Fe}^{\text{II}}(\text{edta})^{2-}$ as Counter-Ions

Fred C. Anson, Jean-Michel Saveant and Kiyotaka Shigehara
J. Amer. Chem. Soc., 105, 1096 (1983)

Electrostatic Binding of Anions and Cations to Graphite Electrodes Coated with a Polyelectrolyte Containing Both Positive and Negative Fixed Charges

Hans-Rudolf Zumbunnen and Fred C. Anson
J. Electroanal. Chem., 152, 111 (1983)

Kinetics of Mediated Electrochemical Reactions at Electrodes Coated with Redox Polymer Films

F. C. Anson, J. M. Saveant and K. Shigehara
J. Electroanal. Chem., 145, 423 (1983)

Kinetics of Electron Transfer Cross-Reactions Within Redox Polymers. Coatings of a Protonated Polylysine Copolymer with Incorporated Electroactive Anions

Fred C. Anson, Takeo Ohsaka and Jean-Michel Saveant
J. Amer. Chem. Soc., 105, 4883 (1983)

Shifts in Redox Formal Potentials Accompanying the Incorporation of Cationic Complexes in Perfluoro Polycarboxylate and Polysulfonate Coatings on Graphite Electrodes

Yu-Min Tsou and Fred C. Anson
J. Electrochem. Soc., in press

New Strategies for Electrocatalysis at Polymer Coated Electrodes. Reduction of Dioxygen by Cobalt Porphyrins Immobilized in Nafion Coatings on Graphite Electrodes

Daniel A. Buttry and Fred C. Anson
J. Amer. Chem. Soc., in press

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